

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 23/78, 37/02, C07C 17/156	A1	(11) International Publication Number: WO 99/34918 (43) International Publication Date: 15 July 1999 (15.07.99)
--	-----------	---

(21) International Application Number: PCT/IB99/00065

(22) International Filing Date: 6 January 1999 (06.01.99)

(30) Priority Data:
98300097.7 8 January 1998 (08.01.98) EP

(71) Applicant (for all designated States except US): EVC TECHNOLOGY AG [CH/CH]; Baarerstrasse 2, CH-6300 Zug (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CARMELLO, Diego [IT/IT]; Via Montecivetta, 8, I-31021 Mogliano Veneto (IT). GARILLI, Marco [IT/IT]; Via Buozzi, 14, I-33170 Pordenone (IT). FATUTTO, Pierluigi [IT/IT]; Riviera Marco Polo, 47, I-30171 Mestre (IT). CACCIALUPI, Letizia [IT/IT]; Localita Caggiolo, 174, I-52010 Subbiano (IT).

(74) Agent: VOTIER, Sidney, David; Carpmaels & Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: CATALYST, PROCESS FOR ITS PREPARATION, AND ITS USE IN THE SYNTHESIS OF 1,2-DICHLOROETHANE

(57) Abstract

A catalyst for the oxychlorination of ethylene to 1,2-dichloroethane is prepared by impregnating a γ -alumina support with a magnesium salt, drying the product, and impregnating the product with a copper salt, preferably together with a lithium salt. The catalyst preferably contains 0.1 to 5 % magnesium, 2 to 10 % copper and 0 to 5 % lithium, by weight, and is particularly effective in oxygen-based processes.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CATALYST, PROCESS FOR ITS PREPARATION, AND ITS USE IN THE SYNTHESIS OF 1,2-DICHLOROETHANE.

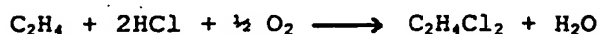
Introduction

5

This invention relates to an industrial catalyst, its preparation, and its use, especially for the production of EDC by the oxychlorination of ethylene in a fluidizable or fixed bed reactor.

10 Background of the invention

The oxychlorination of ethylene to 1,2-dichloroethane (EDC) is known to be catalysed by catalysts containing, inter alia, copper, suitably in the form of its chloride, often in admixture with alkali metal salts, and
15 carried on an alumina support. Such catalysts have been described, as well as the related preparation methods, in several patents. The ethylene oxychlorination reaction



20

exploits a catalyst whose active phase is copper chloride. The first patents claimed a simple catalyst prepared by impregnating a suitable support, often γ -alumina, with a solution containing copper chloride. However, a real development of such catalyst was achieved by adding a
25 further salt, chosen from among the alkali, alkaline-earth or rare-earth metals. Thus, binary, ternary and sometimes quaternary compositions are described in many patents, as well as different preparation methods.

A typical example of a binary composition is described in EP 041330 (PPG) and is a catalyst prepared with copper and potassium chlorides. The claims refer to a real active phase constituted by KCuCl_3 . The method of preparation is based on a co-precipitation of CuCl_2 and KCl on various supports, the preferred one being attapulgite clay. Copper content in the catalyst ranges from 4 to 12% by weight preferably between 7 and 9%.
35 The molar ratio Cu:K is 1:1. Such a catalyst is said to be suitable for fluid bed applications.

European Patent EP 119933 (MONTEPOLIMERI) describes a binary composition based on copper and magnesium, codeposited on the support as chlorides.
40 In this case, the preferred support is $\gamma\text{-Al}_2\text{O}_3$, preferably with a relatively high surface area and proper pore volume. The amount of

copper in the catalyst lies in the range 1-10% by weight, while the magnesium content goes from 0 to 1 mole per mole of copper. The preparation method includes the use of HCl during the dry impregnation procedure.

5

European Patent EP 176432 (AUSIMONT) describes a fluidizable catalyst. Copper and magnesium are the metals used and the crucial item in the preparation method is said to be the radial distribution of the active phase inside the support particles. In fact, a catalyst having less
10 copper on the surface of the particles is claimed, with relevant reduction of sticking phenomena. Copper and magnesium content in the catalyst falls between 1 and 10% by weight, preferably between 2 and 6% for copper.

15 In EP 0278922 (ENICHEM SYNTHESIS) is described a catalyst for fluid bed applications and the method for its preparation based on γ -alumina, Cu and alkali or alkaline earth metals. Copper content ranges from 3 to 7% by weight while from 0.01 to 4% of the aforesaid additives is included. The examples describe a γ - Al_2O_3 -supported catalyst containing Cu and Ca; a
20 catalyst containing also Mg; and a catalyst which includes Li instead of Mg. All the catalysts were prepared by one-shot impregnation, with an aqueous solution of the salts. The oxychlorination reactions are carried out using an air-based process, operating with an oxygen excess.

25 US Patent No. 4,446,249, (GEON) describes the use of a catalyst containing copper on γ -alumina, wherein the support is modified prior to the deposit of copper by incorporating in it from 0.5 to 3.0% by weight, based on the weight of the support, of at least one metal selected from
30 the group consisting of potassium, lithium, rubidium, caesium, alkaline earth metals, rare earth metals and combinations thereof, by admixing a water solution salt of metal(s) with the γ - Al_2O_3 support, drying the mix and calcining it at 350 to 600°C for about 4 to 16 hours. However, in the example in this patent, even though the Cl/C ratio settled is near the
35 the stoichiometric) the HCl conversion to EDC is decidedly low with respect to the usual standard conversion required by and achieved in modern industrial plants (>99%).

US Patent No. 3,624,170 (TOYO SODA) claims a ternary catalytic
40 composition based on CuCl_2 , NaCl and MgCl_2 , the atomic ratio Cu:Na:Mg being 1:0.2-0.7:0.3-1.5. Such catalyst is claimed to avoid the

deactivation caused by contamination due to FeCl_3 present inside the stainless steel reactors.

5 EP-A-0255156 (SOLVAY) describes ternary catalytic compositions containing a mixture of copper chloride, magnesium chloride and an alkali metal chloride which is sodium chloride or lithium chloride, used in precise proportions, which enable a good yield to be achieved in a fluidized bed process for the oxychlorination of ethylene to 1,2-dichloroethane, simultaneously reducing the corrosion of stainless steel reactors as a
10 result, in particular, of a reduction in the sticking and clumping of the particles of catalyst. This document teaches that, for ternary compositions containing copper chloride, magnesium chloride and sodium chloride as an alkali metal chloride, a Na/Cu atomic ratio above 0.2:1 leads to problems of corrosion of the reactor. In contrast, if lithium
15 is used as an alkali metal, no corrosion phenomenon is seen over a wide range of Li/Cu atomic ratios. However, the examples show the appearance of problems of sticking and clumping of the catalyst with compositions containing Li in an Li/Cu ratio above 0.6.

20 Patent US 4,849,393 (GEON) describes catalysts containing, besides copper chloride and an alkali metal salt, a rare earth metal salt. The catalysts contain from about 2% to about 8% by weight of copper, from about 1% to about 10% by weight of a rare earth metal salt and from about 0.25% to about 2.3% by weight of an alkali metal salt. All the salts are
25 co-deposited on a suitable support by means of the dry impregnation procedure, to give a catalyst which allows high ethylene efficiency and low stickiness. In particular, it is stated that, using copper chloride, potassium chloride and one or more rare earth metal chlorides, an excellent catalyst for fluid bed ethylene oxychlorination is obtained.

30 More specific is the composition of the catalyst claimed in EP A 0375202 (ICI), in which is described a ternary catalytic composition based on copper chloride, magnesium chloride and potassium chloride. Copper content ranges from 3 to 9% by weight, while that of magnesium and
35 potassium is from 0.2 to 3%. The preferred atomic ratios Cu:Mg:K are 1:0.2-0.9:0.2-0.9.

US Patent No. 5,260,247 (SOLVAY) describes a quaternary catalytic composition based on CuCl_2 , MgCl_2 , LiCl and at least one other alkali
40 metal chloride on an inert support (Al_2O_3). Also in this patent the support is impregnated with the metal salts in one shot. The examples

refer to an air-based oxychlorination process, operating with an oxygen excess of 36% and a Cl/C ratio of 0.95.

5 The catalytic activity of copper chloride supported on γ -alumina towards the oxychlorination of ethylene to EDC is thus well known and it is also known that several alkali metal salts or alkaline-earth metal salts improve the performance of the catalyst in terms of selectivity and productivity in fixed and fluid bed reactors. In the latter case, the fluidization is particularly critical, especially when the Cl/C ratio is
10 close to 1, because in these conditions the HCl excess induces the phenomenon of stickiness. In the recycle process, where the ethylene is in excess with respect to the HCl, the problem of sticking is negligible and the final target is the maximum HCl conversion achievable operating with a low excess of oxygen, thus maximizing the ethylene yield to EDC.
15 This is also true for fixed bed applications, characterized by a reactant stream very rich in ethylene.

As far as industrial fluid bed oxychlorination reactors are concerned, the main problems are related to: fluidization of the catalyst, abrasion
20 of the reactor, ethylene yield to EDC and EDC productivity. In recycle processes, with which the present invention is particularly concerned, fluidisation of the catalyst is not a problem. Even abrasion of the reactor does not represent a critical item, because γ -alumina is usually used to prepare catalysts for fluid bed applications. However, any
25 improvement in ethylene yield or in productivity is fundamental for an industrial application. It is, therefore the object of the present invention to provide a catalyst which is suitable for any oxychlorination reaction, air- or oxygen-based, and particularly for the oxygen-based process, which operates with vent gas recycle. Such a catalyst must lead
30 to improved ethylene yield and productivity with respect to the existing industrial catalysts.

According to the present invention there is provided a catalyst which is suitable for catalysing the oxychlorination of ethylene to 1,2-
35 dichloroethane, which comprises a γ -alumina support coated with a first layer containing magnesium and, on the first layer, a second layer containing copper and, optionally, lithium.

The invention also provides a process for preparing a catalyst suitable
40 for catalysing the oxychlorination of: ethylene to 1,2-dichloroethane, which comprises impregnating γ -alumina with a solution containing a

magnesium salt, drying the product, and impregnating the product with a solution containing a copper salt and, optionally, a lithium salt.

The catalyst suitably contains, by weight, from 0.1 to 5%, preferably 0.1 to 2%, magnesium; from 2 to 10%, preferably 2 to 8%, copper; and from 0 to 5%, preferably 0 to 1%, lithium. A particularly preferred catalyst contains, by weight, 0.5 to 1.5% magnesium; 3 to 6% copper; and 0.1 to 0.3% lithium.

10 The γ -alumina used as the catalyst support preferably is one having a surface area of from 50 to 220 m²/g, especially 80 to 180 m²/g, and an average particle size in the range 40 to 60 μ m.

In a preferred process for producing the catalyst the γ -alumina is dried, 15 in order to remove water adsorbed inside its pores, and is then impregnated with a solution of a magnesium salt, suitably magnesium chloride. The product is dried, suitably overnight, and it is then impregnated with a solution of a copper salt, suitably copper chloride, either alone or, preferably, in combination with a lithium salt, again 20 suitably as lithium chloride. The product of this second impregnation step is then dried.

By pre-impregnating the γ -alumina with a magnesium salt the acidic centres on the alumina surface are neutralised, forming magnesium 25 aluminate, and are thus unavailable for reaction with the copper. This means that all or substantially all of the copper is available for catalysing the oxychlorination reaction. This is demonstrated by the following solubility tests the results of which are given in Table 1.

30

TABLE 1

SAMPLES	Cu (%w/w) Before Extraction	Cu (% w/w) After Extraction	Mg (% w/w) Before Extraction	Mg (% w/w) After extraction
Cu/Al ₂ O ₃	4	3.52	-	-
Cu/Mg/Al ₂ O ₃	4	2.92	0.75	0.58
Mg/Al ₂ O ₃	-	-	0.75	0.74

35

40

Three catalysts were prepared by impregnating γ -alumina with 1) copper chloride, 2) copper chloride and magnesium chloride, and 3) magnesium chloride. The catalysts were treated with acetone, which is able to dissolve CuCl_2 and MgCl_2 , but not copper or magnesium aluminate, nor the copper hydroxo-complexes, such as paratacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$. The catalyst containing only copper had its metal content reduced from 4 to 3.52%, while the presence of magnesium enhanced the amount of free copper chloride, leaving only 2.92% copper on the catalyst. At the same time, due to the competitive reaction between copper and magnesium to form the aluminate, part of the magnesium was present as chloride and dissolved in acetone, leaving 0.58% of that metal on the catalyst. Such competitive reaction is absent when there is no copper on the catalyst. In fact, all the magnesium added becomes insoluble (sample 3). It is to be noted that the amount of magnesium used for preparing the $\text{Mg}/\text{Al}_2\text{O}_3$ system was the same as was used for preparing the $\text{Cu}/\text{Mg}/\text{Al}_2\text{O}_3$ catalyst.

However, to have a catalyst not only active, but also giving a high productivity, a high dispersion of the active phase is required, i.e. very small crystals should be present all over the support surface. Big agglomerates do not help the catalyst action. Co-precipitation of CuCl_2 and MgCl_2 leads to the formation of macrocrystals, while the presence of lithium chloride produces microcrystals, enhancing the dispersion of the active phase. As a consequence, the preferred preparation method is as follows:

- (i) impregnation of γ -alumina with a solution containing MgCl_2 (dry impregnation procedure);
- (ii) drying at 80°C overnight;
- (iii) second impregnation with a solution containing CuCl_2 and LiCl followed by drying at 80°C overnight;
- (iv) activation of the catalyst at 200°C .

In experimental trials, the activation may be carried out directly inside the fluid bed pilot reactor.

The synergistic effect due to this preparation procedure provides a very efficient catalyst for ethylene oxychlorination, particularly for the oxygen-based process, which operates by recycling the vent gas and with

low oxygen excess and low Cl/C ratios. This synergistic effect represents a substantial advantage over known methods. For example, in US Patent No. 4,446,249 (GEON), which describes a two-steps preparation procedure where the additive(s) are added prior to copper deposition, the method requires a calcination after the first impregnation, so that the support is modified through a reaction between the support and the alkali, alkaline-earth or rare earth metal salt(s). As a consequence, the support which is impregnated with the copper chloride solution has changed. Moreover, besides copper chloride no other salt is present in the solution used for the second dry impregnation.

On the contrary, the present invention is not based on a bulk modification of the support and a following simple impregnation with copper chloride, but rather modifies chemically only the surface of the support by means of magnesium aluminate formation and at the same time enhances the dispersion of copper, deposited in the second step together with lithium, whose ionic dimension induces the formation of highly dispersed small crystals.

The following Examples are given to illustrate, but not to limit, the invention.

Experimental apparatus

All the experimental tests were carried out on the fluid bed pilot plant depicted in Fig. 1.

The core of such plant is the reactor, which is a tube made of nickel, 3m length, with an internal diameter of 40 mm. Reagents flowrates are controlled by mass flow meters through a computer system which also keeps under control the whole pilot plant (pressure, temperature, etc). The products (EDC + water) are collected in a drum after condensation in a water condenser. Moreover, the vent gas from the first condenser undergoes a further cooling by means of a glycol condenser. The final vent gas is neutralized by a caustic washing, but such stream is analyzed by an on-line GC before neutralization. In fact the caustic washing removes the CO₂ present in that stream and this would not allow a correct mass balance. Finally, the amount of vent gas after the caustic column is measured. EDC and water collected in the drum are analyzed to give the EDC purity (identifying the impurities) and detect the amount of HCl unconverted, which dissolves in the water.

Catalyst preparation

All the catalysts were prepared following the dry impregnation procedure, i.e. by adding to the support a volume of solution equal to the total pore volume available.

In all the Examples, the support used for preparing the catalyst was a γ -alumina having a surface area of about 180 m²/g, a pore volume of about 0.5 cc/g and a mean particle size of 45-50 μ m. Such alumina was dried at 120°C for 4 hours before the impregnation, in order to remove the water adsorbed inside the pores. Two kilograms of catalyst were prepared for each Example described below. The impregnation was carried out with solutions containing CuCl₂ and/or MgCl₂ and/or LiCl in amounts which ensure the final compositions reported in Table 2. The equipment used for the dry impregnation procedure was a rotary vessel. After each impregnation, a drying step at 80°C overnight was carried out. The activation was performed at 200°C inside the pilot reactor under nitrogen flow. For all the samples the atomic ratios Cu:Mg:Li are 2:1:1.

Examples 1, 2, 4, 5, 7 and 9 are Comparative Examples.

TABLE 2

EXAMPLE	Cu (% w/w)	Mg (% w/w)	Li (% w/w)	IMPREGNATION
1	4	-	-	Single
2	4	0.75	-	Single
3	4	0.75	-	Double
4	4	-	0.2	Single
5, 7, 9	4	0.75	0.2	Single
6, 8, 10	4	0.75	0.2	Double

Examples 1-6

The catalysts were tested by using them in ethylene oxychlorination reactions carried out at the following operating conditions:

5	temperature	220°C
	pressure:	5 barg
	residence time:	17 seconds
	C ₂ H ₄ flow:	150-160 Nl/h
10	HCl flow:	250-260 Nl/h
	O ₂ flow:	70-75 Nl/h
	N ₂ flow:	240-250 Nl/h

15 The results achieved under the aforesaid operating conditions are shown in Table 3:

20 TABLE 3

25	EXAMPLE	Cl/C Ratio	O/C Ratio	HCl Conv. (%)	Recycle C ₂ H ₄ yield (%)	EDC Purity %	Burning (%)
	1	0.81	0.48	99.59	95.89	99.18	2.39
	2	0.8	0.48	99.83	96.55	99.38	1.97
	3	0.82	0.47	99.56	97.47	99.46	1.43
	4	0.79	0.48	99.93	96.46	99.23	1.9
	5	0.8	0.49	99.86	97.66	99.43	1.25
30	6	0.79	0.48	99.86	97.88	99.48	1.07

From the above results it will be seen that there is a well defined catalyst activity sequence, taking into consideration the recycle ethylene yield as reference parameter. Such sequence is shown below:

5

$\text{Cu} < \text{Cu/Mg(s.i)} \text{ and } \text{Cu/Li} < \text{Cu/Mg (d.i.)} < \text{Cu/Mg/Li(s.i)} < \text{Cu/Mg/Li(d.i)}$

10

Such sequence points out clearly that the effect due to the pre-impregnation with magnesium combined with the co-deposition of copper and lithium on the support is really positive and the synergistic effect associated with the double impregnation is quite evident. The average productivity of the catalyst achieved at these operating conditions is around 535 $\text{g}_{\text{EDC}}/\text{hkg}_{\text{cat}}$.

15

Examples 7-8

20

Such Examples tested in the samples containing Cu, Mg and Li and were carried out to verify the effect of the double impregnation at different operating conditions. Thus, the temperature was increased by 5°C and residence time was reduced by 2 seconds. Such test was devoted to study the catalyst behaviour when reactant flows are enhanced to gain in productivity. To balance the consequent residence time contraction the

25

temperature was raised from 220 to 225°C. The overall operating conditions were:

30

temperature:	225°C
pressure:	5 barg
residence time:	15 seconds
C ₂ H ₄ flow:	170-180 Nl/h
HCl flow:	270-280 Nl/h
O ₂ flow:	75-80 Nl/h
N ₂ flow:	250-260 Nl/h

35

The results achieved under the aforesaid operating conditions are shown in Table 4

TABLE 4

EXAMPLE	Cl/C Ratio	O/C Ratio	ECI Conv. (%)	Recycle C2H4 Yield (%)	EDC Purity (%)	Burning (%)
7	0.77	0.45	99.85	97.28	99.38	1.33
8	0.78	0.45	99.79	97.9	99.42	0.99

The results confirm that the Cu-Mg-Li based catalyst prepared by double impregnation is more efficient also at these operating conditions, reducing the ethylene loss by about 23%. Furthermore, the average productivity of the catalyst achieved is around 593g_{EDC}/hkg_{cat}, that is about 11% higher with respect to Examples 1-6.

Examples 9-10

These tests focused on the catalyst flexibility, i.e. the ability of the catalyst to maintain a certain efficiency when residence time reduces without any increase in temperature. To do that, the reaction temperature was kept constant at 225°C, while residence time was reduced by 1 second with respect to Examples 7 and 8. The operating conditions settled were:

temperature: 225°C
 pressure: 5 barg
 residence time: 14 seconds
 C₂H₄ flow: 180-190 Nl/h
 5 HCl flow: 290-300 Nl/h
 O₂ flow: 80-90 Nl/h
 N₂ flow: 280-290 Nl/h

10 Even in this case, the double impregnation procedure ensures a higher ethylene yield, as shown in Table 5:

15 TABLE 5

EXAMPLE	Cl/C Ratio	O/C Ratio	HCL conv (%)	Recycle C ₂ H ₄ Yield (%)	EDC Purity (%)	Burning (%)
20						
9	0.78	0.45	99.91	97.41	99.4	1.29
10	0.77	0.44	99.96	97.7	99.34	1.1

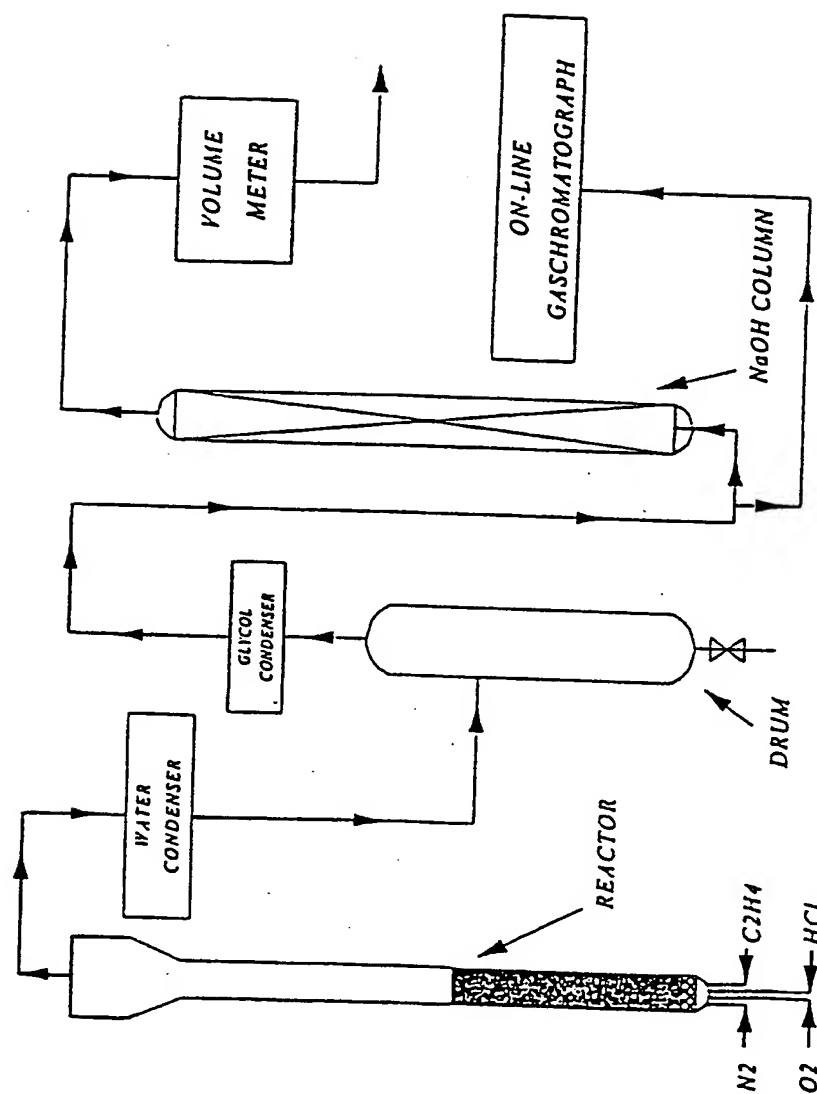
25
 30 The average productivity of the catalyst achieved at these operating conditions is around 648g_{EDC}/h.kg_{cat}, which means an enhancement of ca.21% with respect to Examples 1-6 and ca.9% in comparison with Examples 7-8. Thus, the oxychlorination catalysts of the present invention show substantial advantages over those previously proposed. The benefits
 35 reported in the Examples for pilot scale procedures represent very substantial savings when extrapolated to full-scale industrial production.

CLAIMS

1. A catalyst comprising a γ -alumina support coated with a first layer containing magnesium and, on the first layer, a second layer
5 containing copper and, optionally, lithium.
2. A catalyst as claimed in claim 1 containing, by weight, from 0.1 to 5% magnesium, from 2 to 10% copper, and from 0 to 5% lithium.
10
3. A catalyst as claimed in claim 2 containing, by weight, from 0.1 to 2% magnesium, from 2 to 8% copper, and from 0 to 1% lithium.
4. A catalyst as claimed in claim 3 containing, by weight, 0.5
15 to 1.5% magnesium, from 3 to 6% copper, and from 0.1 to 0.3% lithium.
5. A catalyst as claimed in any of claims 1 to 4 wherein the γ -alumina has a surface area of from 50 to 220 m²/g and an average particle size in the range 40 to 60 μ m.
20
6. A catalyst as claimed in claim 5 wherein the γ -alumina has a surface area of from 80 to 180m²/g.
7. A process for preparing a catalyst which comprises impregnating
25 γ -alumina with a solution containing a magnesium salt, drying the product, and impregnating the product with a solution containing a copper salt and, optionally, a lithium salt.
8. A process as claimed in claim 7 wherein the salts are the chloride
30 salts.
9. A catalyst produced by the process of claim 7 or 8.
10. A process for the catalytic gas phase oxychlorination of ethylene
35 which comprises reacting ethylene, hydrogen chloride and a source of oxygen in the presence of a catalyst as claimed in any of claims 1 to 6 and 9.

1 / 1

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 99/00065

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J23/78 B01J37/02 C07C17/156

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 971 996 A (THE DISTILLERS COMPANY) 7 October 1964 see claims 1-5	1-4, 7-10
X A	EP 0 176 432 A (AUSIMONT SPA) 2 April 1986 see claim 5	1-10 2-6
A	US 4 460 699 A (CONVERS RONALD J ET AL) 17 July 1984 see claim 6	1-10
A	US 4 451 683 A (DAVIES PHINEAS ET AL) 29 May 1984 see column 1, line 29 - column 2, line 36	1-6, 10
A	WO 81 01284 A (GOODRICH CO B F) 14 May 1981 see page 4, line 20 - line 32	1, 7, 10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 April 1999

Date of mailing of the international search report

03/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Faria, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Patent Application No

PCT/IB 99/00065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 971996 A		BE 636856 A DE 1443708 A FR 84193 E NL 131716 C NL 297252 A	20-03-1969 17-03-1965
EP 0176432 A	02-04-1986	BR 8504512 A CA 1248934 A DE 3564911 A JP 1808116 C JP 5016904 B JP 61086951 A MX 166997 B US 4871707 A	15-07-1986 17-01-1989 20-10-1988 10-12-1993 05-03-1993 02-05-1986 22-02-1993 03-10-1989
US 4460699 A	17-07-1984	NONE	
US 4451683 A	29-05-1984	AU 548739 B AU 7926682 A BR 8200180 A CA 1187066 A EP 0057796 A FI 820105 A GR 76385 A IE 52463 B IN 157542 A JP 1592251 C JP 2014101 B JP 57136943 A TR 21784 A ZA 8200088 A	02-01-1986 22-07-1982 09-11-1982 14-05-1985 18-08-1982 16-07-1982 06-08-1984 11-11-1987 19-04-1986 14-12-1990 06-04-1990 24-08-1982 01-05-1985 24-11-1982
WO 8101284 A	14-05-1981	AR 223552 A AU 539334 B AU 6576980 A BE 885929 A BR 8008903 A CA 1151636 A EP 0039723 A IN 151951 A JP 3039740 B JP 56501440 T KR 8302154 A PT 72014 A, B US 4446249 A	31-08-1981 20-09-1984 22-05-1981 16-02-1981 25-08-1981 09-08-1983 18-11-1981 10-09-1983 14-06-1991 08-10-1981 17-10-1983 01-12-1980 01-05-1984